



Integration of biomass pretreatment with fast pyrolysis: An evaluation of electron beam (EB) irradiation and hot-water extraction (HWE)

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ABSTRACT

Integration of biomass pretreatment with pyrolysis offers an opportunity to improve end-product quality and conversion efficiency. In this study, sugar maple (*Acer saccharum*) was subjected to both hot-water extraction (HWE) at 160 °C (at residence times of 0.5 h, 1.0 h, and 2.0 h) and electron beam (EB) irradiation at a dose of 1000 kGy. Pyrolysis studies were then conducted on all the treated samples at 550 °C using a bench scale pyroprobe-gas chromatography–mass spectrometry (Py-GC/MS). The HWE samples were selected for further evaluation in catalytic pyrolysis using HZSM-5 catalysts for the production of aromatic hydrocarbons. Analysis of the hot-water treated sample at 160 °C for 2 h showed that HWE increased the volatile matter and decreased the fixed carbon and ash contents; also the glucan content increased by 24% and the xylan decreased by 54%. Derivative thermogravimetry (DTG) analysis indicated that EB irradiation reduced the crystallinity of the sugar based polymers while HWE solubilized the hemicellulose fraction. The pyrolysis results showed that EB irradiation increased the formation of furanic aldehydes (furfural and 5-hydroxymethylfurfural (5-HMF)) and decreased hydroxyacetaldehyde (HAA) and levoglucosan (LG). By contrast, HWE increased the yield of LG, HAA, 5-HMF and furfural; but, decreased the yields of acetic acid (HAc), hydroxyacetone, and other ketones. For the HWE-2 h sample, LG formation increased from 4.45 wt.% to 11.57 wt.% and HAc decreased from 4.87 wt.% to 2.40 wt.%. Catalytic pyrolysis of HWE samples with HZSM-5 zeolite showed that the carbon yields of monoaromatic hydrocarbons increased. HWE treatment at 160 °C for 2 h increased the yield of benzene by 46%, toluene by 35% and xylene by 26%. Pyrolysis-TGA also indicated that HWE decreased the formation of char/coke. Overall, the reduction in the formation of acids and ketones caused by HWE suggest that it could be used to improve bio-oil quality in non-catalytic pyrolysis whilst the increase in the yield of monoaromatic hydrocarbons indicate that HWE could be used to enhance the carbon efficiency in catalytic pyrolysis.

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1. Introduction

Biomass pretreatment is an important tool for modifying the structural component of lignocellulosic feedstocks to facilitate conversion pathways for the production of biofuels. Over the years, methods such as steam explosion, dilute acid, ammonia fiber explosion (AFEX), liquid hot water, wet oxidation, and CO₂ explosion [1,2] have been explored primarily in biochemical conversion processes to overcome the recalcitrant nature of lignocellulosic and eventually enhance breakdown/conversion of fermentable sugars into bioethanol. Nonetheless, pretreatment could equally play a role in enhancing thermochemical conversion of biomass

into fuels and chemicals. Therefore, there is growing interest in pretreating biomass into a suitable feedstock prior to pyrolysis and gasification with the objective to improve end-product quality and conversion efficiency.

As is well known, the production of bio-oils with desirable fuel properties from conventional pyrolysis is a challenge. The oils are usually acidic, dense, unstable, and viscous. This is fundamentally due to the molecular makeup of the bio-oils. Therefore, ongoing research in the field is focused on addressing the quality of bio-oil to enable its utilization for further processing into hydrocarbon liquid fuels and chemicals. Toward this goal, pretreatment could be used to some extent as a tool to modify the composition/structure of biomass into a suitable feedstock that results in less formation of undesirable components responsible for the detrimental properties of pyrolysis oil. Importantly, the formation of acids and other reactive destabilizing oxygenates must be inhibited or

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minimized during biomass pyrolysis. The carboxylic acids (e.g. acetic acid) produced due to deacetylation of hemicellulose [3] which render pyrolysis oil corrosive [4] and also promote aldol condensation reactions during storage [5] need to be significantly reduced or completely removed. Aldehydes and other carbonyl containing species would equally have to be eliminated since they are believed to be responsible for polymerization or condensation reactions [5] which cause increase in viscosity and phase separation during storage. Therefore, it would be beneficial if appropriate pretreatments could be integrated with biomass pyrolysis to increase the selectivity into producing more desirable products. Additionally, pretreatment can be close coupled with catalytic pyrolysis to improve carbon efficiency of the upgrading technology. The challenge is to identify suitable pretreatment options that could be intergraded with pyrolysis since direct transfer of pretreatment methods used in biochemical conversion to thermochemical platform may not necessarily lead to expected outcomes.

Currently, the major pretreatment methods that have been explored in biomass pyrolysis include acid washing [6], mild acid hydrolysis [7], chemical treatment [8], hydrothermal/hot-water treatment [9–12], torrefaction [13–18], steam explosion [19], and hydrothermal carbonization [20]. Among these methods, torrefaction, which is a thermal pretreatment (200–300 °C) has particularly received extensive attention in recent years. Studies show that torrefaction is able to improve the quality of bio-oil to a certain degree by decreasing the total acid number and the oxygen content of the oil [16]. However, some studies suggest that torrefaction also has detrimental effects on pyrolysis. It has been found that torrefaction at high temperatures decreases the bio-oil yield and increases the char yield [13,16–18]. The decrease in the overall liquid yield from torrefied biomass has been attributed to cross-linking and carbonization of the torrefied biomass [13,17,18]. On the other hand, studies on preprocessing techniques such as hydrothermal [9] and hydrolysis [11] suggest that pretreatment may not significantly improve the conversion efficiency of pyrolysis/catalytic pyrolysis. From these previous findings, it can be inferred generally that biomass pretreatment could either have a negative or positive impact on pyrolysis. Hence, further investigations on other potential techniques are needed to assist in identifying biomass pretreatments that could be well suited for pyrolysis integration.

In this present work, the concept of improving the quality of pyrolysis oil using hot-water extraction (HWE) and electron beam irradiation pretreatments was evaluated. Their influences on the chemical composition of the pyrolysis vapors were investigated. The HWE process employs hot-water without the addition of mineral acids/bases at a moderate temperature (160 °C). This pretreatment has been demonstrated to selectively solubilize the hemicellulose fraction [21]. An attractive aspect of the HWE pretreatment technology is that, it fits into a biorefinery concept where structural polymers that may be undesirable in pyrolysis for instance, could be extracted and used as high value chemical platforms for the production of fuels and chemicals in a suitable conversion process other than pyrolysis [22]. As illustrated in Fig. 1, the HWE process produces organic rich extracts which can be recovered/processed independent of pyrolysis into value added chemicals such as furfurals and acids. Also, water-soluble inorganic earth elements (i.e. K, Ca, Mg and P) which complicate biomass pyrolysis are removed in the HWE pretreatment step. The electron beam (EB) pretreatment on the other hand is an industrially proven technology which has wide use in applications such as curing of coatings and inks, crosslinking of rubber, recycling of plastics, and etc. [23]. EB irradiation has been demonstrated to decrystallize and depolymerize cellulose and hemicellulose by bond cleavage. Additionally, chemical bonds and linkages between lignin and hemicellulose are broken during EB irradiation. In a study by Driscoll et al. [28], they found that molecular weight of

Table 1

Characteristics of sugar maple and HWE-2.0 h treated feedstock.

Analysis	Biomass feedstocks	
	Sugar maple	^a HWE-2.0 h treated sample
<i>Proximate analysis (wt.% dry basis)</i>		
Volatile matter (VM)	85.56	88.05
Fixed carbon (FC)	13.63	11.57
Ash	0.81	0.38
<i>Ultimate analysis (wt.% dry basis)</i>		
Carbon	48.91	49.79
Hydrogen	5.87	5.95
Nitrogen	<0.5	<0.5
Sulfur	<0.05	<0.05
Chlorine (ppm)	69	262
Oxygen (by difference)	44.39	43.86
<i>Compositional analysis (wt.% dry basis)</i>		
Glucan	39.44	48.92
Xylan	15.91	7.38
Acetyl	3.76	1.2
Arabinan	0.23	0
Mannan	2.27	1.24
Total lignin	26.33	27.45
Water extractable others	3.63	5.28
Ethanol extractives	1.27	5.12

^a Hot water extraction conducted at 160 °C for 2 h

microcrystalline cellulose (MCC) could be reduced from 82,000 to 2200 Da after 1000 kGy (kiloGray) irradiation while reducing the crystallinity of MCC from 87 to 45%. Also, Cheng et al. (2013) showed that EB pretreatment of maple wood at doses in the range of 250–100 kGy can increase the rate and yield of glucose sugar produced by a mixture of cellulases by 3–5 fold compared to untreated controls. The effect of HWE and EB on the composition/structure of biomass could consequently alter the formation of oxygenates during pyrolysis. Thus, in this study, we evaluated the ability of HWE and EB in increasing the selectivity of forming desirable oxygenates during pyrolysis.

2. Materials and methods

2.1. Biomass feedstocks

The biomass samples were supplied by the State University of New York College of Environmental Science and Forestry (SUNY-ESF). Sugar maple samples were obtained from ESF's Heiberg Forest in Tully, NY and debarked by hand prior to chipping. All samples were chipped on a commercial wood chipper, dried, ground in a Thomas-Wiley mini-mill (Thomas Scientific), and sized to 60 mesh (250 µm). The moisture content of biomass samples before each test was determined using MJ33 compact infrared moisture analyzer (Mettler Toledo, Greifensee, Switzerland). Proximate and ultimate analysis of each feedstock shown in Table 1 was performed by Galbraith Analytical Laboratory (Knoxville, TN, USA). Compositional analysis (carbohydrates, lignin, and extractives) in Table 1 was performed by Microbac Laboratories, Inc. (Boulder, CO, USA) according to NREL Laboratory Analytical Procedures (LAP).

2.2. Biomass preprocessing

The debarked sugar maple was subjected to hot-water extraction (HWE) pretreatment at 160 °C for 0.5 h, 1.0 h, and 2 h. A 4:1 ratio of water to biomass was used for the extraction in a 6 L M/K digester with a centrifugal pump for liquor circulation and a PID temperature controller. After extraction, the samples were washed and air dried for storage. The EB pretreatment was conducted on both the control and the 2 h-HWE sugar maple samples. The EB irradiation pretreatment was performed in a 3.0 MeV, 50/75 mA

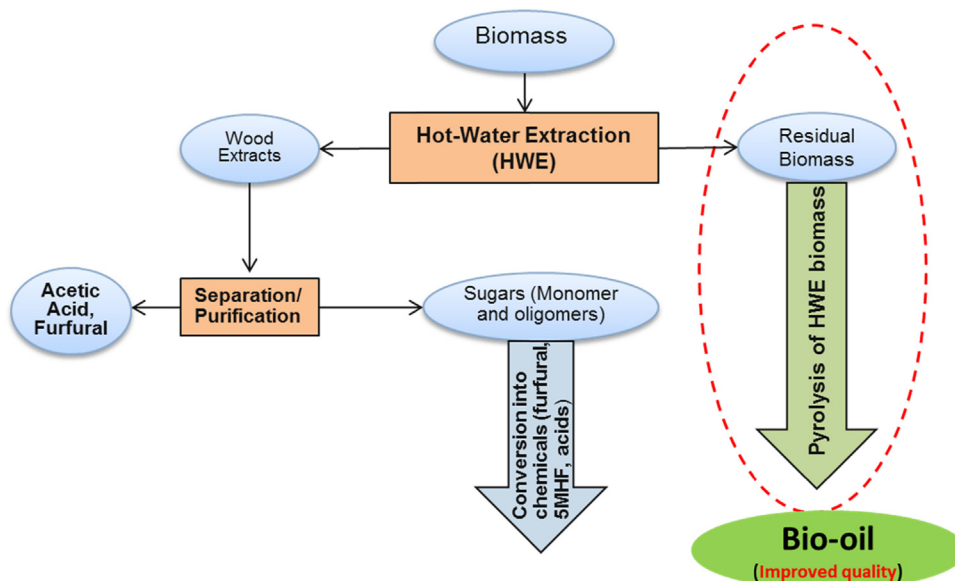


Fig. 1. Conceptual integration of HWE step with pyrolysis in a biorefinery.

250 kW Dynamitron Accelerator (IBA Industrial Inc., formerly Radiation Dynamics Inc.) located at Edgewood, NY. For the experiment, 100 g of biomass samples were packed in polyethylene plastic pouches and were placed on a conveyor moving at a speed of 3 m/min. The sample was then EB irradiated in air at 125 kGy per scan. Scanning was done multiple times to achieve 1000 kGy total dosages of exposure. EB irradiation dose was determined by a thin film dosimeter to ensure that all the samples received a similar effective dose.

2.3. ZSM-5 zeolite catalysts

A commercial HZSM-5 zeolite (Süd-Chemie Incorporated) was obtained from Utah State University for catalytic pyrolysis studies. The HZSM-5 powder was calcined at 550 °C for 5 h in a muffle furnace before testing. The measured surface area was 325 m²/g and the average bulk density was 0.50 g/cm³.

2.4. Thermogravimetric analysis

The biomass samples were first subjected to thermogravimetric analysis in a TA Instruments Q50 TGA. About 5 mg of each biomass sample was heated at 20 °C/min from 25 °C to 750 °C with 60 mL/min of nitrogen as carrier gas.

2.5. Pyrolysis/catalytic pyrolysis-GC/MS experiments

The pyrolysis of the control and the pretreated samples were conducted using a CDS Analytical Pyroprobe 5200 (CDS Analytical, PA) interfaced with Agilent 7890A gas chromatograph and 5975C mass spectrometer detector. Detailed description of the experimental set has been reported in a previous study [24]. A Mettler Toledo MS105 semi-micro-balance with sensitivity of 0.01 mg (Mettler Toledo, Greifensee, Switzerland) was used to weigh samples of sizes between 0.3 and 0.6 mg into a quartz tube reactor of 25 mm in length and 1.9 mm in diameter. The loaded sample in the quartz tube was held in place at the center with small plugs of quartz wool. The pyrolysis experiments were performed at 550 °C and for 20 s. For the catalytic pyrolysis experiments, untreated and HWE treated samples were placed in between two beds of HZSM-5 catalysts at both ends of the quartz tube reactor. The catalyst-to-

feed (CF) ratio was about 10 (w/w). Each experimental run was conducted at least five times to ensure reproducibility and accuracy of results. A 60 m × 0.25 mm DB-1701 capillary column of 0.25 μm film thickness was used for the separation of products. The GC inlet was set to 275 °C and a split ratio of 75:1 was used. The column followed a temperature program of 40 °C for 1 min, 6 °C/min to 130 °C, 10 °C/min to 275 °C held for 20 min. Column flow was controlled to maintain a constant linear velocity of 1 mL/min. The ion source and the interface of the mass spectrometer detector were held at 230 °C and 250 °C respectively. Electron ionization of the compounds was performed at 69.9 eV and the ions were separated by their mass-to-charge (*m/z*) ratios in the range of 28–350. Pure compounds purchased from Sigma–Aldrich were used for calibration, confirmation and quantification of key products from biomass pyrolysis. The National Institute of Standards and Technology (NIST) mass spectral library was also used in support of the custom library created from the mass spectra of the calibrated compounds. Analytical standards of the pure compounds for the calibration of the GC/MS system were prepared in accordance to ASTM method D4307. For each compound, a linear calibration curve was established for concentrations of 250, 750, 1250, 2500 and 5000 μg/mL. The calibration curves had *R*² value greater than 0.95. Table 2 shows the main pyrolysis products that were quantified.

3. Results and discussion

3.1. Biomass characteristics

Table 1 shows the proximate, ultimate, and compositional analyses of sugar maple (control) and the HWE-2.0 h (160 °C for 2 h) treated sample. From the data, it can be seen that HWE pretreatment at 160 °C for 2 h improved the fuel property of the sugar maple feedstock as evidenced by the increase in volatile matter (VM) and decrease in ash content. Consequently, the fixed carbon (FC) decreased upon treatment. The FC and ash of the control were 13.6 wt.% and 0.81 wt.% respectively. In contrast, the HWE-2.0 h feedstock had FC of 11.6 wt.% and ash content of 0.38. Consequently, the volatile matter (VM) in HWE-2.0 h (88.1 wt.%) was higher than the control (85.6 wt.%). Based on the ash analysis, it can be inferred that HWE at 160 °C for 2 h removed over 50% of the inorganic elements (e.g. Si, K, Ca, K, Mg, Na, Fe). The removal of the alkali and

Table 2

Major pyrolysis decomposition products from untreated sugar maple and HWE treated samples.

Quantified (selected pyrolysis compounds)	Yield (wt.% dry basis)			
	Control-sugar maple	HWE-0.5 h	HWE-1.0 h	HWE-2.0 h
<i>Carbohydrate decomposition products</i>				
Hydroxyacetaldehyde	11.76	13.16	12.66	12.43
Levogluconan	4.45	6.30	3.74	11.57
Acetic acid	4.87	4.53	3.39	2.40
Hydroxyacetone	1.23	1.03	0.92	0.82
Methyl pyruvate	0.97	0.86	0.74	0.71
Furfural	0.44	0.59	0.54	0.51
5-Hydroxymethyl furfural	0.43	0.58	0.66	0.71
5-Methylfurfural	0.03	0.04	0.03	0.06
2-Furanone	0.37	0.30	0.25	0.23
2-Furanmethanol	0.11	0.10	0.08	0.02
3-Methyl-1,2-cyclopentanedione	0.39	0.19	0.15	0.13
Methanol		0.51	0.41	0.34
Furan		0.08	0.06	0.08
Total	24.91	28.27	23.63	30.01
<i>Lignin decomposition products</i>				
4-Allyl-2,6-dimethoxyphenol	0.44	0.44	0.40	0.38
Syringol	0.24	0.19	0.17	BDL
Syringaldehyde	0.23	0.33	0.26	0.23
Trimethoxybenzene	0.21	0.23	0.19	0.26
2-Methoxy-4-vinylphenol	0.17	0.17	0.09	0.14
Coniferyl alcohol	0.29	BDL	BDL	BDL
Trans-isoeugenol	0.12	0.12	0.08	0.13
3,5-Dimethoxyacetophenone	0.14	0.11	0.07	0.08
Vanillin	0.10	0.14	0.12	0.14
3,5-Dimethoxy-4-hydroxyacetophenone	0.10	BDL	0.10	BDL
Creosol	0.06	0.13	0.14	0.15
Guaiacol	0.05	0.09	0.10	0.11
Total	2.15	1.95	1.72	1.62

BDL, below detection limit.

alkaline earth metals is desirable since their presence in biomass have been shown to have adverse effect on pyrolysis [25,26]. It is worth mentioning that the extent of removal of the individual elements by water extraction however varies from one metal to the other. For example, Chang et al. [10] found that hydrothermal pretreatment of eucalyptus wood at 190 °C significantly removed K, Mn, and Mg metals compared to Ca, Fe, and Al. Additionally, Mourant et al. [27] found out that biomass washing with deionized water removes K, Mg, and Na without difficulty than calcium. Overall, their works show that water extraction is effective in the removal of inorganic species with the exception of calcium which has been reported to be less susceptible to water treatment. This implies that the catalytic effect of Ca may still be evident on the thermal degradation of the HWE pretreated biomass.

The organic elemental compositions show that C, H, N, O were comparable to some extent in all the HWE samples. In contrast, the chlorine content of HWE-2.0 h was higher. The notable increase in the chlorine content after HWE treatment was most likely caused by the tap water used in the extraction. Furthermore, the compositional analysis of the samples shows that the HWE-2.0 h had higher cellulose content (glucan) and a slightly higher lignin fraction. It can be seen that the glucan content increased from 39.4 wt.% to 49 wt.%. By contrast, the content of xylan, arabinan, mannan, and acetyl in the HWE-2.0 h were lower than the control. This was due to selective solubilization of hemicellulose at the conditions employed in the study. Overall, the results suggest that the HWE pretreatment preserved the cellulose and the lignin fractions to a large extent. Fig. 2 is a typical example of the mass balance of the structural components before and after hot-water extraction of sugar maple chips at 160 °C for 2 h with water-to-feed ratio of 4 [21]. It can be seen from the distribution that about 77% by weight of the starting biomass is retained whilst 23% by weight goes into the extract

stream. It should be pointed out that the extract stream is acidic (usually of pH about 3.5) and consisted mainly of xylose, xylose oligomers, acetic acid, and small but recoverable amounts of furfural, methanol, formic acid, and HMF [21]. Importantly, the extract can be considered as a source of high-value chemicals and other biofuel platform molecules.

Unlike the HWE treatment, EB irradiation was done in the solid state and as a result, the amount of the structural components of biomass (hemicellulose, cellulose, and lignin) typically do not change appreciably although each component is depolymerized to varying degrees at dosages up to 1000 kGy. This was shown by Sundar et al. [23]. In their study, they used NIR and chemometric models to show that EB-treated samples at 250, 500, 750, and 1000 kGy had comparable composition of cellulose, hemicellulose, and lignin fractions. This observation was attributed to the fact that the EB irradiation did not result in breakdown of the biomass into lower molecular weight products. Hence, in this study, the EB-treated samples were not subjected to compositional analysis.

3.2. Thermogravimetric analysis (TGA)

The thermogravimetric (TG) and differential thermogravimetric (DTG) curves in Figs. 3 and 4 show the effect of HWE and EB irradiation on the thermal decomposition of sugar maple. It can be seen in the TG profile shown in Fig. 3a that HWE treatment generally caused a slight increase in the formation of solid residue. Fig. 3b show the effect of HWE pretreatment on the major structural components of sugar maple. As shown in the DTG profiles, most of the decomposition occurred between 200 °C and 400 °C. For lignocellulosic biomass in general, the maximum decomposition rate (shoulder peak) between 200 and 280 °C is due to hemicellulose while the intense peak with the maximum rate of decomposition

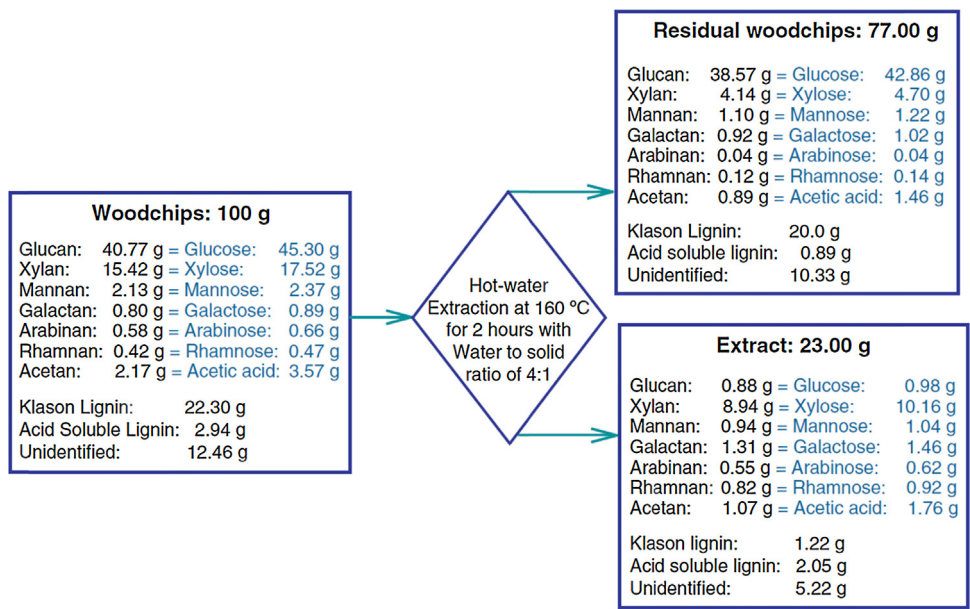


Fig. 2. Typical mass distributions of the major components of sugar maple before and after hot-water extraction.

Adapted from [21].

between 300 and 400 °C is indicative of cellulose. Lignin decomposition, on the other hand, is difficult to identify in a DTG curve of biomass since its thermal breakdown occurs over a broad temperature range and has a low rate of decomposition. In this study, the

hemicellulose peak for the control (untreated sugar maple) was around 285 °C and that of cellulose was at 366 °C. With that in mind, it can be seen that the HWE pretreatment decreased the maximum rate of decomposition at 285 °C with increase in treatment

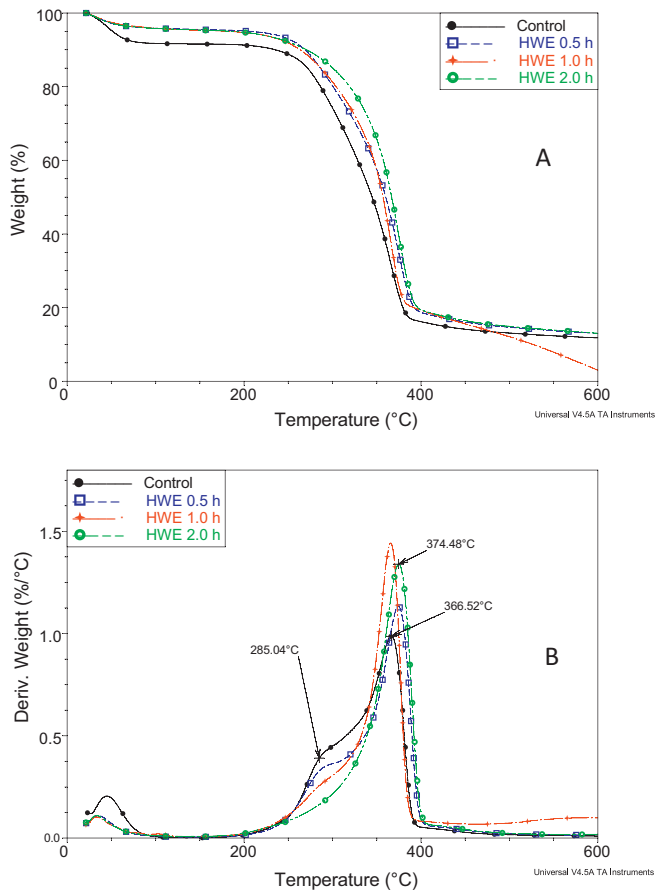


Fig. 3. (A) Thermogravimetric (TG) and (B) differential thermogravimetric (DTG) curves of untreated sugar maple (control) and 3 treated sugar maples (HWE-0.5 h, HWE-1.0 h, and HWE-2.0 h).

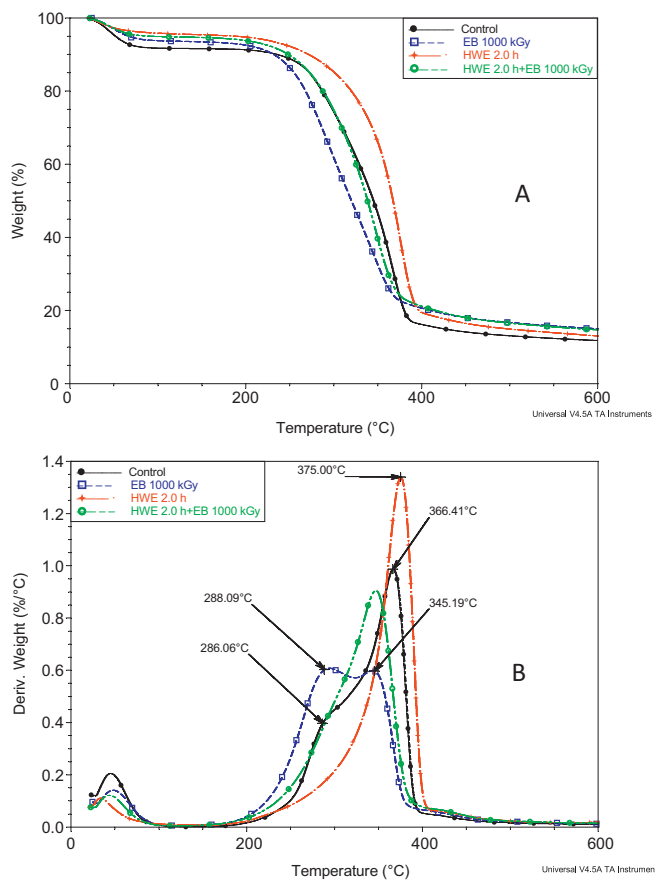


Fig. 4. (A) Thermogravimetric (TG) and (B) differential thermogravimetric (DTG) curves of untreated sugar maple (control) and 3 treated sugar maples (EB 1000 kGy, HWE-2.0 h, HWE-2.0 h + EB 1000 kGy).

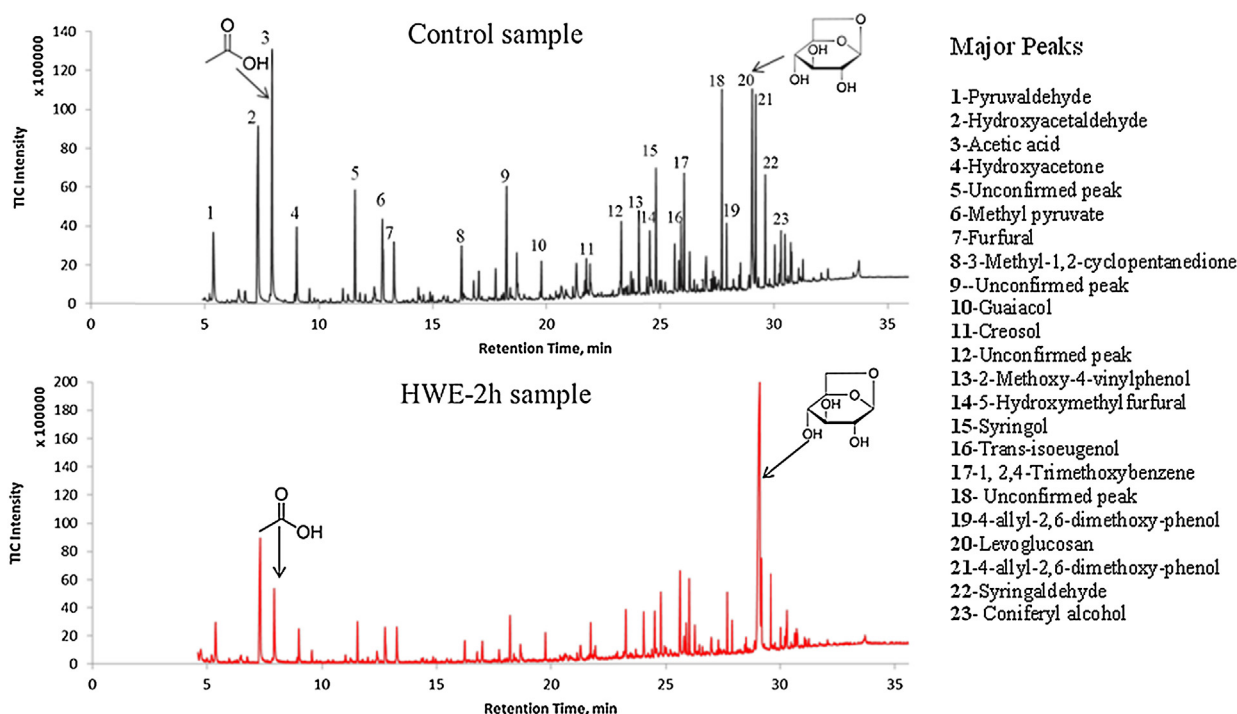


Fig. 5. Py-GC/MS pyrogram showing the effect of HWE on the pyrolysis oxygenates from sugar maple.

residence time. Consequently, the maximum rate of cellulose decomposition rate increased. This confirms that hemicellulose is selectively removed to a large extent during HWE pretreatment as a result of autohydrolysis. It is also worth pointing out that the DTGs for the samples treated at residence times of 0.5 h and 2 h both had the maximum rate of decomposition of cellulose occurring at a slightly higher temperature (374 °C). This could mean that HWE at those conditions affected the structure of cellulose in a different way. Therefore, the shift in the maximum decomposition rate of cellulose to a higher temperature is probably as a result of increase in the crystallinity of cellulose. Interestingly, this was not observed for the treated sample at a residence time of 1 h, rather it had the same temperature for the maximum rate of cellulose decomposition as the untreated sample.

The TG curve in Fig. 4a equally shows that EB treated increased the formation of solid residue. The DTG curves in Fig. 4b however contrasts the effect of EB irradiation and HWE treatments on the rate of decomposition of the biopolymers. It can be seen that EB treatment clearly increased the maximum rate of the decomposition step at 286 °C and conversely decreased the maximum rate of decomposition of the peak between 340 and 380 °C. Additionally the decomposition peaks shifted to a much lower temperature. From the DTG curves, it appears as if the hemicellulose content increased and the cellulose fraction decreased after EB treatment, but that is not a possible reason for the changes observed. As reported, EB irradiation causes cleavage of the cellulose/hemicellulose/lignin chains which consequently lead to a reduction in degree of polymerization and crystallinity [28]. Hence, the EB treated samples could be considered to have relatively more amorphous material than the control. For these reasons, the increase in rate of decomposition at 286 °C after EB treatment with dosage of 1000 kGy was attributed to amorphous cellulose decomposition. On the other hand, the decrease in the maximum rate of decomposition for the cellulose peak between 340 and 380 °C is because of reduction in the crystalline cellulose caused by EB. The treatment of the HWE-2.0 h sample with EB irradiation even sheds more light on the effects of the electron-beams. From the DTGs

of the samples (HWE-2.0 h sample and HWE 2.0 h + EB 1000 kGy), it can be observed that the maximum rate of decomposition of the cellulose at 375 °C decreased and the new peak occurred at a lower temperature after EB treatment. Consequentially, the profile showed that the peak broadened afterwards. This again is because amorphous regions increased after EB treatment. These observations are in fact consistent with the findings by Poletto et al. [29] and Kim et al. [30] on the influence of cellulose crystallinity on thermal decomposition of wood.

Overall, it can be inferred from the TGA that both HWE and EB pretreatments affect the physicochemical properties of the structural components. Both methods altered the thermal degradation of sugar maple and caused an increase in the formation of solid residue. In short, HWE mainly reduced the hemicellulose fraction and increased the relative content of cellulose. On the other hand, EB irradiation caused chain cleavage of the structural biopolymers and lowered the thermal decomposition temperature of sugar maple.

3.3. Effect of HWE pretreatment on pyrolysis oxygenates from sugar based polymers

The primary objective of this work was to evaluate the appropriateness of HWE and EB as pretreatments options for improving the selectivity of pyrolysis by minimizing the formation of undesirable oxygenates. The characteristics in Table 1 and the DTG profiles in Fig. 1a indicated that HWE affected the physicochemical properties of the sugar maple biomass. Equivalently, GC/MS quantitative analysis of selected oxygenates in Table 2 showed that HWE consequently influenced pyrolysis intermediates. The HWE resulted in both, increase and decrease in the yields of individual oxygenated species. Based on the quantitative GC/MS analysis, it can be seen that the treated samples overall gave slightly higher yields than the control with the exception of one at residence time of 1.0 h.

The GC/MS pyrogram in Fig. 5 shows the effect of HWE on a number of pyrolysis oxygenates produced from sugar maple. The major carbohydrate decomposition products that increased upon

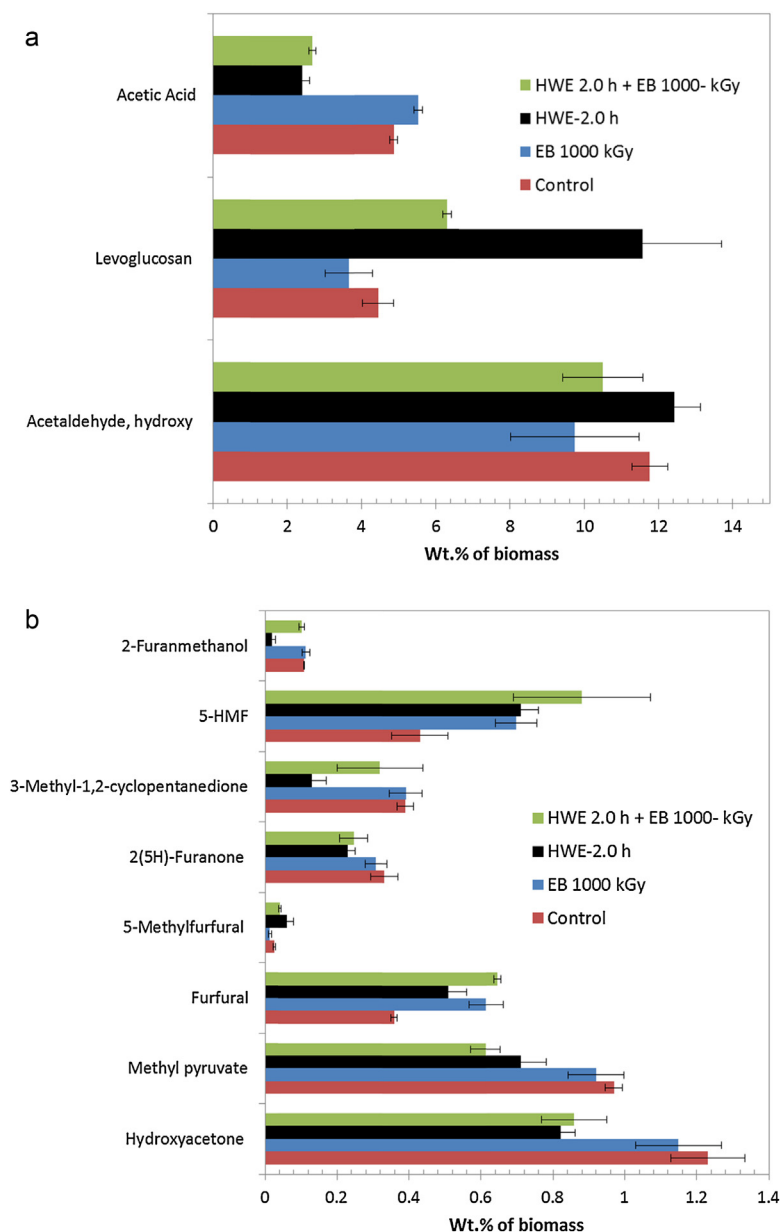


Fig. 6. (a) Product distribution chart showing the effect of EB irradiation pretreatment on the formation of hydroxyacetaldehyde, acetic acid and levoglucosan. Red, untreated sugar maple; Blue, sugar maple treated with 1000 kGy EB (max dose) in nitrogen; Black, hot-water extracted sugar maple at 160 °C for 2 h; and Green: sugar maple treated by hot water extraction (160 °C) then EB treated at 1000 kGy in nitrogen. (b) Product distribution chart showing the effect of EB irradiation pretreatment on the formation of hydroxyacetone, methyl pyruvate, furfural, 5-methyl furfural, 5-HMF, 2(5H)-furanone, 3 methyl-1,2-cyclopentanedione, and 2-furanmethanol. Red, untreated sugar maple; Blue, sugar maple treated with 1000 kGy EB (max dose) in nitrogen; Black, hot-water extracted sugar maple at 160 °C for 2 h; and Green, sugar maple treated by hot water extraction (160 °C) then EB treated at 1000 kGy in nitrogen. (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)

HWE pretreatment were: levoglucosan (LG), hydroxyacetaldehyde (HAA), 5-hydroxymethylfurfural (5-HMF), and furfural. On the other hand, the products that decreased were as follows: acetic acid (HAc), hydroxyacetone (HA), methyl pyruvate (MP), 2-furanone, and 2-methyl-1,2-cyclopentanedione. Largely, the increase in some of the oxygenated species was attributed to an increase in the relative cellulose fraction. Concomitantly, the decrease seen in other pyrolysis organics was attributed to a decrease in hemicellulose content after HWE treatment.

Importantly, it can be seen from the data in Table 1 that increase in extraction severity resulted in a decrease in HAc yield. HWE pretreatment at residence time of 2.0 h reduced the yield of HAc from 4.87 wt.% to 2.40 wt.%. That is 50% decrease in the formation of acetic acid. In pyrolysis, HAc is produced largely from the

cleavage of acetyl groups attached to the xylan backbone in the cell wall of lignocellulosic biomass. Consequently, the removal of acetyl groups/xylan by HWE pretreatment would eventually result in a feedstock that produces less carboxylic acid such as acetic acid. In contrast to LG formation, the yield of HAc gradually decreased with increase in HWE residence time. The effect of HWE on the yield of HAc is desirable as it could be used as a tool to reduce the acidity of pyrolysis oils. Furthermore, to improve fuel quality, it is important to decrease the formation of carbonyl groups as they are known to cause instability issues [5]. From the results, it can be seen that HWE decreased most of the ketones which originate from hemicellulose decomposition. For instance, the yield of hydroxyacetone reduced from 1.23 wt.% to 0.82 wt.%. Nonetheless, increases in the formation of other carbonyls such as aldehydes were observed. To

Table 3

Major pyrolysis decomposition products from lignin showing the effect of EB pretreatment.

Quantified (Selected pyrolysis compounds)	Yield (wt.% dry basis)			
	Control-sugar maple	EB 1000 kGy	HWE-2.0 h	HWE-2.0 h + EB 1000 kGy
<i>Lignin decomposition products</i>				
4-Allyl-2,6-dimethoxyphenol	0.44	0.52	0.38	0.52
Syringol	0.24	0.29	BDL	0.32
Syringaldehyde	0.23	0.15	0.23	0.30
Trimethoxybenzene	0.21	0.26	0.26	0.35
2-Methoxy-4-vinylphenol	0.17	0.19	0.14	0.17
Coniferyl alcohol	0.29	BDL	BDL	BDL
Trans-isoeugenol	0.12	0.18	0.13	0.15
3,5-Dimethoxyacetophenone	0.14	0.14	0.08	0.07
Vanillin	0.10	0.12	0.14	0.12
3,5-Dimethoxy-4-hydroxyacetophenone	0.10	0.05	BDL	0.05
Creosol	0.06	0.14	0.15	0.21
Catechol	BDL	0.10	BDL	0.16
Guaiacol	0.05	0.13	0.11	0.16
Total	2.15	2.27	1.62	2.58

BDL, below detection limit.

have a significant impact on the physical property of the resulting pyrolysis oil, the aldehydes would have to be decreased significantly since they are produced in higher quantities than ketones during pyrolysis. Particularly, HAA was produced in yields between 11 and 13 wt.% and happens to be the highest single oxygenate formed during pyrolysis. Its formation is well known to be by ring cleavage of the cellulose monomer with subsequent rearrangement of the two-carbon fragments. Typically, this thermal decomposition pathway is promoted by the presence of inorganic compounds and lignin [31]. That being the case, one may expect that the formation of HAA would decrease upon pretreating sugar maple by HWE since about 50% of the inorganics were removed. However, that was not observed under the pyrolysis conditions used in this study. Nevertheless, it appears HWE could be optimized to alter the mechanism of cellulose degradation to produce other aldehydes instead of HAA. As an example, 5-HMF is produced competitively from ring-opening and rearrangement reactions of cellulose. Thus, HWE could potentially be used to promote this pathway. A good reason to enhance the formation of furanic aldehydes (5-HMF and furfural) instead of HAA is that they are relatively less oxygenated.

Furthermore, it can be seen that, LG which is a major depolymerization product of cellulose pyrolysis was significantly increased by the HWE-2 h treatment. The yield from the control sample was 4.45 wt.% and that from the HWE-2 h sample was 11.57 wt.%. This indicates that, the formation of levoglucosan increased by a factor of 2.6 after HWE for 2 h. The significant increase in LG was attributed to the increase in the relative cellulose content in the treated samples. Another factor that could contribute to the increase in formation of LG is the reduced amount of inorganic matter present in the HWE samples relative to the control. It is believed that the removal of alkaline cations in biomass enhances the depolymerization of the cellulose chain over fragmentation reactions [32]. Additionally, other factors such as the degree of polymerization of the cellulose influence the formation of LG [31]. In a study by Wang et al. [33], they found that highly crystalline cellulose produces higher yields of LG at pyrolysis temperatures above 300 °C when compared to amorphous cellulose. This may explain why the HWE-1.0 h sample in particular produced a lower yield of LG relative to the other HWE samples. As shown in the TGA studies, the temperature for the maximum rate of decomposition of cellulose for this sample (HWE-1.0 h) was different from the other treated HWE samples. It can be recalled that the maximum rate of cellulose decomposition for the HWE-1 h occurred at a lower temperature which may indicate that the degree of crystallinity of its cellulose was relatively lower.

3.4. Effect of EB irradiation on pyrolysis oxygenates

Fig. 6a and b shows the effect of EB treatment on selected primary pyrolysis oxygenates from carbohydrate while products from lignin degradation are shown in Table 3. From the results, it can be observed that exposure of the samples to EB irradiation at 1000 kGy affected some of the pyrolysis product yields. As shown in the bar charts, the yields of levoglucosan, hydroxyacetaldehyde, methyl pyruvate, and hydroxyacetone generally decreased after EB treatment. In the case of the HWE-2 h sample, EB irradiation caused about 45% reduction in LG and 15% decrease in HAA yields. On the contrary, oxygenates such as 5-HMF and furfural predominately increased in yields. The yield of 5-HMF increased by 62% and furfural by 71% after EB irradiation of the control (See Fig. 6a and b). The yields of acetic acid and 3-methyl-1,2-cyclopentanedione were found to increase slightly as well. For acetic acid, EB caused a 13% increase after treatment in the case of the control sample, and 11% for the HWE-2 h sample.

As previously discussed, EB treatment is known to cause chain depolymerization and decrystallization. Thus, the effects seen particularly with the yields of LG, and the furan derivatives can be attributed to EB-induced micro-structural changes within the polysaccharides. Consequently, the results suggest that crystallinity and DP of cellulose play a role in the formation of these products. Therefore, it appears that crystalline cellulose yields more LG and amorphous cellulose forms more furfurals. The data from both HWE and EB treatments affirm this notion. Moreover, it is in agreement with other research reports. For example, Cabradilla and Zeronian [34] found that crystalline cellulose enhances the formation of LG. Recently, Wang et al. [33] also studied the effect of cellulose crystallinity on the product distribution during pyrolysis. In that study, it was found that, at temperatures higher than 350 °C, crystalline cellulose tend to produce a higher amount of LG whilst amorphous cellulose forms considerably higher amount of furanic compounds (5-HMF, 5-methyl furfural, furfural, and furanones). Additionally, the relatively high yields of 5-HMF and furfural produced by the EB treated samples are consistent with the work by Ponomarev et al. [35] in which they showed that electron-beam distillation of natural polymers enhances the formation of furfurals.

The slight increase in acetic acid suggests that EB enhanced deacetylation of the acetyl groups attached to the xylan backbone. More importantly, it should be noted that EB chain scissions could increase carboxyl and carbonyl groups in the pyranose structure which may be an additional source for the formation of acetic acid [36].

As shown in this study, EB irradiation reduced some oxygenates with carbonyl functionalities (e.g. hydroxyacetaldehyde, hydroxyacetone, methyl pyruvate, and furanone) which can be considered as a desirable effect in terms of bio-oil quality; however, the overall yield of oxygenated species was lower for the treated samples. It is therefore important that the reduction in yields of undesirable oxygenates correlates with the yields of desirable products so as to have a positive effect on the conversion efficiency. This implies that the yields of 5-HMF and furfural that improved after EB treatment would have to increase dramatically to offset the loss in yields from other oxygenates. Further, these furanic compounds are considered to be platform molecules for the production of hydrocarbon fuel and thus are more desirable than other linear aldehydes in pyrolysis oil. Alternatively, EB pretreatment could be used prior to HWE to enhance any positive synergistic effects. For instance, since EB cleaves carbonyl and carboxyl groups, its use prior to HWE pretreatment may facilitate the removal of carboxylic and carbonyl groups during the HWE step. With such a concept, the pyrolysis of the HWE treated feedstock would result in higher organic yield and higher quality pyrolysis oil. Based on the outcome of the EB studies, it appears that electron beam irradiation has potential for improving the selectivity of biomass pyrolysis by minimizing the formation of reactive carbonyls and maximizing the formation of furfurals. Additionally, since EB decreases the onset temperature and activation energy of pyrolysis, it could improve the thermal conversion process. Nevertheless, further studies are needed to ascertain thoroughly its suitability for pyrolysis and to enhance the advantages shown in this work. This will require determination of optimal EB treatment conditions for biomass pyrolysis. Also, appropriate pyrolysis operating conditions for EB treated biomass would have to be investigated since EB affects the thermal decomposition of the biomass.

3.5. Effects of HWE and EB pretreatments on decomposition products from Lignin

Comparison of the phenolic yields in the quantitative GC/MS analyses shown in Tables 2 and 3 suggest that the pretreatments also affected lignin decomposition products. Overall, it can be seen that HWE decreased the yields of the phenolics. By contrast, EB irradiation seems to increase the yield of the phenolics. The results suggest that the minimal degradation of lignin that occurs during HWE affected primarily these phenolics: syringol, conifer alcohol, and dimethoxyacetophenones. Nevertheless, it is unclear why the HWE caused a decrease in the yields of phenolics since the compositional analysis showed that the relative content of the lignin was not affected. In general, the formation of the phenolics from lignin during pyrolysis is by free-radical reactions as a result of cleavages of the different linkages (mainly α - or β -O-4 aryl ether bonds) between the phenylpropane units. This means that electron-beam irradiation which causes chain scission could in fact enhance the cleavages of the various bonds. This may explain why the phenolic yields for the EB treated samples were relatively higher. The most effect in phenolics yield change was seen when the HWE-2.0 h sample was exposed to EB irradiation. The quantitative GC/MS analysis show that the overall yield of the selected phenolics increased from 1.62 wt.% to 2.58.

Ideally, it would be desirable to produce phenolics with less functionality and of lower molecular weight (LMW), because the multifunctional nature of most of the phenolics contributes to the instability of bio-oils and also increase the bio-oil's viscosity since it is of higher molecular weight (HMW). With both treatments, it can be seen that defunctionalization was not promoted as a result, thus the yields of monomeric phenolics with relatively LMW such as catechol and guaiacol were

still low. Nonetheless, Ponomarev et al. [35] found that EB distillation of lignin actually increased the yield of guaiacol and creosol. This account suggest that EB has the potential to promote the formation of LMW phenolics during pyrolysis, but the pretreatment condition for that to happen would have to be identified.

3.6. Effects of HWE on catalytic fast pyrolysis using HZSM-5 zeolite

HWE was exclusively evaluated in the catalytic pyrolysis of sugar maple for the production of aromatic hydrocarbons. Fig. 7a shows the Py-GC/MS results for the carbon yields of benzene, toluene, ethylbenzene, and xylene. The bar chart shows that HWE increased the yields of these monoaromatic hydrocarbons. Comparison between the yield from the control and the HWE-2 h sample indicated that HWE pretreatment increased the yield of benzene by 46%, toluene by 35% and xylene by 26%. The yields of other identified hydrocarbons such as alkylbenzenes, naphthalenes, and indenes which were identified with the NIST library were not quantified due to the fact the GC column was not calibrated with their standards. Nevertheless, the peaks areas of the aromatics were compared as shown in Fig. 7b. The results indicate that the distribution of aromatics produced from the control was comparable to the HWE samples. This suggests that the selectivity of the aromatic hydrocarbons was not affected by the HWE pretreatment. It can also be inferred from the peak area distribution that naphthalenes and xylenes were the highest aromatics produced, followed by toluene and substituted benzenes. Polycyclic aromatic hydrocarbons and benzene were the lowest fraction produced.

The increase in the actual yield of the monoaromatic hydrocarbons due to HWE treatment as shown by the quantitative GC/MS analysis (Fig. 7a) was attributed to the increased content of cellulose in the HWE samples. Since there was not any difference in the selectivity of the aromatics, it implies that all the samples formed common intermediates, but in different quantities. As shown in Table 2, the overall yield of oxygenates quantified from the HWE-2 h sample was higher than the control. Therefore, it means more primary intermediates were available for conversion in the catalytic step with HZSM-5. Generally, cellulose is known to produce higher yields of volatiles than hemicellulose or lignin. Thus, the high yield of monoaromatics from the HWE samples is because their cellulose fractions were relatively higher than the control. In fact, a recent study by Wang et al. [37] on catalytic pyrolysis of individual components of lignocellulosic biomass using HZSM-5 reported that the yield of aromatic hydrocarbons decreased in the order of cellulose > hemicellulose > lignin. This infers that cellulose has high selectivity for hydrocarbons; thus feedstocks with higher cellulose content would tend to produce more aromatics.

Further studies performed by pyrolysis-TGA with ZSM-5 catalysts on the HWE samples clearly indicated that the HWE pretreatment to a certain degree does not increase char/coke formation (Fig. 7c). It can be seen that the untreated biomass had the highest weight of residue and spent catalyst; thus indicating that the untreated sample forms more char/coke yield. However, it should be mentioned that high pretreatment severity has the potential to increase the yield of coke. Among the pretreated samples, the weight of residue and spent catalyst after the TGA-pyrolysis followed this order; HWE-2.0 h > HWE 1.0 h > HWE-0.5. This means pretreatment at low severity (160 °C for 0.5 h) significantly reduces the yield of coke formation. Overall, the outcome of the study suggests that HWE pretreatment close-coupled with catalytic fast pyrolysis could improve the carbon efficiency.

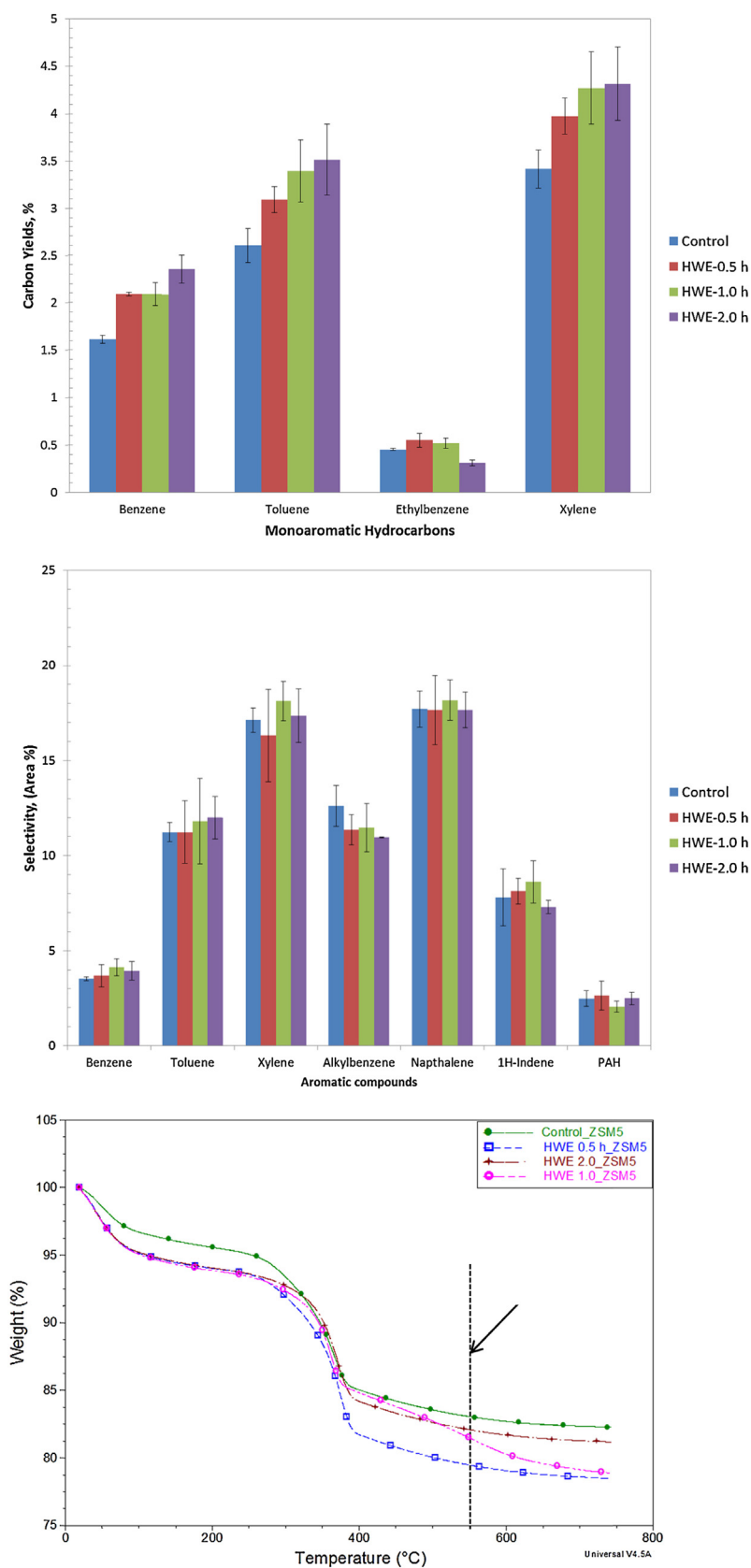


Fig. 7. (a) Carbon yields of benzene, toluene, ethylbenzene, and xylene produced from the catalytic pyrolysis of sugar maple-control and the three HWE samples (HWE-0.5 h, HWE-1.0 h, and HWE-2.0 h). (b) Selectivity of the aromatic hydrocarbons based on peak areas generated for the sugar maple-control and the three HWE samples (HWE-0.5 h, HWE-1.0 h, and HWE-2.0 h) in the catalytic pyrolysis with HZSM-5 catalyst. (c) TG curves of catalytic pyrolysis of sugar maple-control and the three HWE samples (HWE-0.5 h, HWE-1.0 h, and HWE-2.0 h) showing the effect of HWE treatment on the formation of char/coke.

4. Conclusion

This preliminary work evaluated the concept of close-coupling hot-water extraction (HWE) and electron beam (EB) irradiation pretreatments with biomass pyrolysis. The purpose was to study these preprocessing methods as tools for modifying the composition of pyrolysis vapors with the interest of reducing the formation of carboxylic acids and carbonyls which are known to make bio-oils corrosive and unstable. The findings show that HWE produces a modified feedstock with higher cellulose and lignin contents due to solubilization of hemicellulose. It was shown that EB irradiations at dosages up to 1000 kGy depolymerized cellulose and hemicellulose components to varying degrees. The most obvious finding that emerged from this study is that that HWE could be used to reduce the formation of carboxylic acids and ketones whilst improving the yield of organics. Nonetheless, it was found that HWE is unable to decrease the formation of hydroxyacetaldehyde (HAA) which is the highest carbonyl compound found in bio-oil. The results also show that EB irradiation has the potential to increase the formation of useful furanic aldehydes (furfural and 5-hydroxymethylfurfural (5-HMF) and decrease the yield of HAA. An implication of the EB irradiation study is the possibility that it can be used to alter primarily the decomposition of sugar based polymers to produce furan type oxygenates. With respect to lignin decomposition products, HWE was found to decrease the yields of phenolics; by contrast, EB irradiation caused an increase in the yield of the phenolics. Another major finding was that HWE increased the carbon yields of hydrocarbons produced in the ZSM-5 based catalytic pyrolysis without affecting the selectivity of the aromatic hydrocarbons. The present study adds to a growing body of literature on integration of biomass pretreatment with thermochemical conversion as a way of enhancing carbon efficiency and product quality.

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